

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 302 994 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 158(3) EPC

(43) Date of publication:

16.04.2003 Bulletin 2003/16

(51) Int Cl.7: **H01M 4/38**, H01M 4/02,
H01M 10/40

(21) Application number: **01948051.6**

(86) International application number:
PCT/JP01/06189

(22) Date of filing: **17.07.2001**

(87) International publication number:
WO 02/007239 (24.01.2002 Gazette 2002/04)

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

(30) Priority: **19.07.2000 JP 2000218528**

(71) Applicant: **MATSUSHITA ELECTRIC INDUSTRIAL
CO., LTD.**

Kadoma-shi, Osaka 571-8501 (JP)

(72) Inventors:

- **SATO, Toshitada**
Osaka-shi, Osaka 538-0044 (JP)

- **BITO, Yasuhiko**
**Miharacho, Minamikawachi-gun, Osaka 587-
(JP)**
- **OKAMURA, Kazuhiro**
Hirakata-shi, Osaka 573-0013 (JP)
- **NITTA, Yoshiaki**
Hirakata-shi, Osaka 573-1122 (JP)

(74) Representative: **Nachshen, Neil Jacob et al**
D Young & Co
21 New Fetter Lane
London EC4A 1DA (GB)

(54) NON-AQUEOUS ELECTROLYTE SECONDARY CELL

(57) A non-aqueous electrolyte secondary battery containing an alloy particle capable of absorbing and desorbing lithium in the negative electrode has a short cycle life and is insufficient in high-rate discharge characteristics, since the alloy particle is pulverized during charge/discharge cycles. In order to solve this problem, a negative electrode is employed, which comprises an alloy particle containing: at least two selected from the

group consisting of metal elements and semimetal elements; oxygen; and nitrogen. It is preferred that the alloy particle have a phase A capable of electrochemically absorbing and desorbing lithium ion and a phase B having lithium ion conductivity or lithium ion permeability and that the phase B contain larger amounts of oxygen and nitrogen than the phase A.

EP 1 302 994 A1

BEST AVAILABLE COPY

Description

Technical Field

5 [0001] The present invention relates to non-aqueous electrolyte secondary batteries: More specifically, the present invention relates to a non-aqueous electrolyte secondary battery including an improved negative electrode, and having high capacity, long life and excellent high-rate discharge characteristics.

Background Art

10 [0002] In the positive electrode for a non-aqueous electrolyte secondary battery, chalcogenides such as LiMn_2O_4 , LiCoO_2 , LiNiO_2 , V_2O_5 , Cr_2O_5 , MnO_2 , TiS_2 and MoS_2 may be employed. They have a layered or tunneled structure permitting the intercalation and deintercalation of lithium ion.

15 [0003] On the other hand, metallic lithium may be employed in the negative electrode for a non-aqueous electrolyte secondary battery. In this case, a battery of high energy density and high voltage can be realized. However, the use of metallic lithium results in lithium dendrites deposited on the surface of the metallic lithium during charging, which may reduce the charge and discharge efficiency, or cause an internal short-circuit due to the contact between the dendrites and the positive electrode. Therefore, graphite-based carbon materials which have lower capacity than metallic lithium but are capable of reversibly absorbing and desorbing lithium, have recently been employed in the negative electrode. Then, lithium ion secondary batteries which are excellent in cycle characteristics and safety have been put into practical uses.

20 [0004] However, the practical capacity of the carbon material is as small as 350 mAh/g, and the theoretical density of carbon material is as low as 2.2 g/cc. Therefore, alloy particles capable of yielding a negative electrode having higher capacity are desired to be used as the negative electrode material.

25 [0005] However, an alloy is generally pulverized by its repeated expansion and contraction due to the intercalation and deintercalation of lithium ion. The pulverized alloy loses the contact with other alloy particles, conductive agent and the like in the negative electrode, reducing the conductivity of the negative electrode. In other words, the pulverized alloy appears to be an inactive material, so that the capacity of the battery is reduced.

[0006] In view of the above-described problems, the following proposals have been made.

30 [0007] Japanese Unexamined Patent Publication No. hei 11-86854 proposes to allow a phase capable of absorbing lithium and a phase incapable of absorbing the same to coexist in an alloy particle that is the negative electrode material. In a charged state, the phase incapable of absorbing lithium relaxes the expansion stress of the phase capable of absorbing lithium, so that the pulverization due to the expansion of the particle can be suppressed.

35 [0008] Japanese Unexamined Patent Publication No. hei 11-86853 proposes to allow two or more types of phases each capable of absorbing lithium to coexist in an alloy particle that is the negative electrode material. Although the both phases expand at the time of lithium absorption, the expansion stress of the respective phases are different from each other; therefore, the pulverization of the particle can be suppressed by narrowing the difference of the expansion coefficient between the two phases. The respective phases are present as fine crystal grains within the particle. It is considered that the stress is dispersed on the interfaces between the crystal grains at the time of lithium absorption.

40 [0009] However, even a negative electrode material in line with the above proposals is not sufficient to suppress the pulverization and to prevent the degradation of the cycle characteristics due to repeated charging and discharging. The possible reasons are as follows.

45 [0010] According to the former proposal, the expansion coefficients of the respective phases are significantly different from each other. Therefore, uneven stress is produced in the particle, causing a strong partial stress. The phase incapable of absorbing lithium is not able to sufficiently relax this stress. For this reason, it is considered that the particle is eventually pulverized and separated from the conductive network. In addition, the phase incapable of absorbing lithium prevents the movement of lithium ion, so that the high-rate discharge characteristics of the battery are not sufficient.

50 [0011] According to the latter proposal, the both phases absorb lithium ion and thus the difference of the expansion coefficient between the phases is small at the time of lithium absorption. However, the volume expansion of the entire particle is large and, therefore, it is likely that a gap is formed between particles or between a particle and a current collector thereby to deteriorate the current collection. For this reason, it is considered that alloy particles are more likely to be separated from the conductive network in the negative electrode. In other words, according to the latter proposal, it is difficult to suppress a reduction in discharge capacity during charge/discharge cycles, although it is possible to suppress the pulverization of the alloy particles due to the expansion and contraction.

55 [0012] On the other hand, there is also a proposal to employ metal oxides as the negative electrode material.

[0013] For example, Idota et al. proposes a negative electrode containing a tin oxide and having high capacity as well as long life (Science, 276, 5317, 1395-1397 (1997)). However, in the process of the initial charging, it is necessary

to reduce bivalent or tetravalent tin in the tin oxide to a metallic state of zero valent. Accordingly, the irreversible capacity of the battery increases, resulting in an increased amount of lithium which does not participate in charge/discharge cycles. Therefore, only those batteries having low capacities can be obtained.

[0014] As described above, batteries using negative electrodes comprising conventional alloys and oxides have the problem that they are easily degraded in cycle characteristics and tend to have a decreased capacity.

Disclosure of Invention

[0015] It is an object of the present invention to provide a non-aqueous electrolyte secondary battery having high capacity, long cycle life and excellent high-rate discharge characteristics.

[0016] The present invention relates to a non-aqueous electrolyte secondary battery comprising: a positive electrode capable of absorbing and desorbing lithium ion; a negative electrode capable of absorbing and desorbing lithium ion; and a non-aqueous electrolyte containing a lithium salt, the negative electrode comprising: an alloy particle containing at least two selected from the group consisting of metal elements and semimetal elements; and one selected from the group consisting of oxygen and nitrogen, wherein the alloy particle has a phase A capable of electrochemically absorbing and desorbing lithium ion and a phase B which is incapable of electrochemically absorbing and desorbing lithium ion and has lithium ion conductivity or lithium ion permeability and wherein the total of an oxygen content Wao and a nitrogen content Wan is less than 0.5 wt% in the phase A and the total of an oxygen content Wbo and a nitrogen content Wbn is not less than 1.0 wt% in the phase B. As the semimetals, Si, Sb and the like may be used.

[0017] It is preferred that the phase A contain at least one selected from the group consisting of Sn, Si, Al, Ga, In, Pb, Sb and Bi.

[0018] It is preferred that the phase B contain at least one selected from the group consisting of Ti, Zr and rare earth elements.

[0019] It is preferred that the phase A be surrounded by the phase B.

[0020] It is preferred that the oxygen content Wao and the nitrogen content Wan in the phase A and the oxygen content Wbo and the nitrogen content Wbn in the phase B satisfy $\{(Wbo+Wbn)/(Wao+Wan)\} > 4$.

[0021] It is preferred that an oxygen content Wo and a nitrogen content Wn in the alloy particles satisfy $0 < Wo < 10$ wt%, $0 < Wn < 10$ wt% and $0.5 \text{ wt}\% \leq Wo + Wn \leq 10 \text{ wt}\%$.

[0022] The alloy particles may further contain at least one selected from the group consisting of fluorine, sulfur and phosphorous. In this case, it is preferred that the total of a content Wf of at least one selected from the group consisting of fluorine, sulfur and phosphorous, the oxygen content Wo and the nitrogen content Wn be 0.5 to 10 wt% in the alloy particles. Additionally, it is preferred that the Wf be 0.5 to 1 wt%.

Brief Description of Drawings

[0023]

FIG. 1 is a vertical sectional view of a test cell used for evaluating the capacity characteristics of alloy particles in accordance with the present invention.

FIG. 2 is a vertical sectional view of a cylindrical battery comprising alloy particles in accordance with the present invention.

Best Mode for Carrying Out the Invention

[0024] The present invention suppresses the pulverization of a negative electrode material comprising alloy particles due to the expansion and contraction, by the action of a phase B containing at least one selected from the group consisting of oxygen and nitrogen and having lithium ion conductivity or lithium ion permeability. It is considered that, when the phase B has lithium ion conductivity, the phase B has at least lithium ion permeability.

[0025] It is preferred that a phase A contain at least one element selected from the group consisting of Sn, Si, Al, Ga, In, Pb, Sb and Bi (hereinafter, referred to as "group A element"). Group A elements are those elements that are easy to electrochemically form an alloy with lithium. In the case of a lithium secondary battery which employs a negative electrode comprising a group A element, the amount of lithium absorption is large and a high capacity can be achieved.

[0026] It is preferred that the content of a group A element be not less than 50 mol% in the phase A.

[0027] It is preferred that the phase B comprise at least one element selected from the group consisting of Ti, Zr and rare earth elements (hereinafter, referred to as "group B element"). As the rare earth elements, for example, La, Ce and the like may be used.

[0028] Group B elements hardly react with lithium but have high reactivity with oxygen and nitrogen. Therefore, when a group A element and a group B element coexist in the presence of oxygen and nitrogen, the oxidation reaction and

nitriding reaction of the group B element preferentially occur, whereas the oxidation reaction and nitriding reaction of the group A element are suppressed. When the above reactions occur in a state in which the group A element and the group B element either form an intermetallic compound or are fused, a low crystalline or amorphous phase B comprising fine crystal grains is formed since the group A element and the group B element are in a finely dispersed state to a sufficient degree. Accordingly, in the phase B, many grain boundaries are formed and no long-range order of atomic arrangement is observed. An alloy particle having such phase B has good plasticity, so that the pulverization of the phase A is difficult to occur. Moreover, it is possible to obtain alloy particles having good lithium ion conductivity and, therefore, a battery having good high-rate discharge characteristics can be realized.

[0029] It is preferred that the content of a group B element be 5 to 70 wt% in the alloy particle, from the viewpoint of ensuring the capacity. It is also preferred that the content be 5 to 30 wt%, from the viewpoint of ensuring the capacity, cycle life and high-rate discharge characteristics.

[0030] Although group A elements also react with oxygen and nitrogen, the reactivity is far lower than that of group B elements. Therefore, the amounts of lithium ions absorbed in and desorbed from the phase A are not reduced.

[0031] On the assumption that the phase B contains no group B element, oxygen and nitrogen similarly react not only with the phase B but also with the phase A in the presence of oxygen and nitrogen. Consequently, large amounts of oxides and nitrides are produced in the phase A to reduce the amounts of lithium absorbed in and desorbed from the phase A, thereby decreasing the capacity.

[0032] It is preferred that the phase A be surrounded by the phase B in the alloy particle.

[0033] Such structure of the alloy particle allows the stress generated by the expansion and contraction of the phase A to be effectively dispersed, thereby enhancing the effect of suppressing the pulverization.

[0034] It is preferred that an oxygen content W_{ao} and a nitrogen content W_{an} in the phase A, as well as an oxygen content W_{bo} and a nitrogen content W_{bn} in the phase B satisfy $\{(W_{bo}+W_{bn})/(W_{ao}+W_{an})\} > 4$. In the case of $4 \geq \{(W_{bo}+W_{bn})/(W_{ao}+W_{an})\}$, the oxygen and nitrogen contents increase in the phase A, so that the irreversible capacity during the initial charging becomes large.

[0035] From the viewpoint of the balance of the discharge capacity, life characteristics and high-rate discharge characteristics, it is preferred that the oxygen content W_o and the nitrogen content W_n in the alloy particles satisfy $0 < W_o < 10$ wt%, $0 < W_n < 10$ wt% and $0.5 \text{ wt}\% \leq W_o + W_n \leq 10 \text{ wt}\%$. When $W_o + W_n$ is less than 0.5 wt%, the effect of suppressing the pulverization and improving the high-rate discharge characteristics of the present invention is reduced. On the other hand, when $W_o + W_n$ exceeds 10 wt%, the irreversible capacity during the initial charging increases, which decreases the discharge capacity. Also, when the alloy particles excessively contain oxygen and nitrogen, the active material density is decreased, resulting in a decreased volume energy density. Therefore, it is most preferred that $1 \text{ wt}\% \leq W_o + W_n \leq 5 \text{ wt}\%$ be satisfied.

[0036] The alloy particle may comprise at least one selected from the group consisting of fluorine, sulfur and phosphorous, in addition to at least one selected from the group consisting of oxygen and nitrogen.

[0037] Fluorine, sulfur and phosphorous are selectively incorporated into the phase B, rather than into the phase A. When fluorine, sulfur or phosphorous is incorporated into the phase B, a fluoride, a sulfide or a phosphide is produced within the phase B. This improves the lithium ion conductivity or lithium ion permeability even further, thereby yielding excellent high-rate discharge characteristics.

[0038] In order to obtain a superior effect of suppressing the pulverization, it is preferred that the total of the content of at least one selected from the group consisting of fluorine, sulfur and phosphorous, the oxygen content and the nitrogen content be 0.5 to 10 wt%, more preferably, 1 to 5 wt% in the alloy particles.

[0039] To achieve a great effect of the stress relaxation by the phase B while preventing a decrease in the amounts of lithium absorbed in and desorbed from the phase A, it is preferred that not less than 70 wt% of the total amount of at least one selected from the group consisting of fluorine, sulfur and phosphorous, oxygen and nitrogen contained in the alloy particles be contained in the phase B.

[0040] Oxygen and nitrogen can be incorporated into the alloy by utilizing a process such as a gas atomization process, water atomization process or mechanical alloying process, while adjusting the amounts thereof. Similarly, at least one selected from the group consisting of fluorine, sulfur and phosphorous may be incorporated into the alloy.

[0041] In the following, the present invention will be concretely described by reference to examples.

Examples

[0042] Firstly, test cells and cylindrical batteries for evaluating alloy particles in accordance with the present invention are described.

(i) Test cell

[0043] Test cells were used for evaluating the capacity characteristics of alloy particles.

[0044] The test cell shown in FIG. 1 was fabricated.

[0045] 7.5 g of negative electrode alloy particles, 2 g of graphite powder as a conductive agent and 0.5 g of polyethylene powder as a binder were mixed to prepare a negative electrode mixture. 0.1 g of this mixture was press-formed so as to have a diameter of 17.5 mm, thereby producing a test electrode 1. The test electrode 1 was placed in a case 2. Then, a microporous separator of polypropylene 3 was placed on the test electrode 1.

[0046] A mixed solution of ethylene carbonate and dimethoxyethane at a volume ratio of 1:1 with 1 mol/L LiClO_4 dissolved therein was injected into the case 2 as a non-aqueous electrolyte.

[0047] The opening of the case 2 was sealed by a sealing plate 6, having metallic lithium 4 with a diameter of 17.5 mm attached to the inner surface thereof as well as a polypropylene gasket 5 disposed on the periphery thereof, thereby completing a test cell.

(ii) Cylindrical battery

[0048] Cylindrical batteries were used for evaluating the high-rate discharge characteristics and cycle life.

[0049] The cylindrical battery shown in FIG. 2 was fabricated.

[0050] $\text{LiMn}_{1.8}\text{Co}_{0.2}\text{O}_4$ as a positive electrode active material was synthesized by mixing Li_2CO_3 , Mn_2O_3 and CoCO_3 at a predetermined molar ratio and heating the mixture at 900°C . The positive electrode active material was sieved into not larger than 100 mesh.

[0051] To 100 g of the above positive electrode active material were added 10 g of carbon powder as a conductive agent, an aqueous dispersion containing 8 g of polytetrafluoroethylene as a binder and a proper amount of pure water, and the whole was sufficiently mixed to give a paste. The obtained paste was applied to an aluminum core, which was then dried and rolled to produce a positive electrode 11. To the positive electrode core, a positive electrode lead 14 made of aluminum was connected by ultrasonic welding.

[0052] Meanwhile, alloy particles, graphite powder as a conductive agent and styrene butadiene rubber as a binder were mixed at a weight ratio of 70:20:10, and the mixture thus obtained was added with a proper amount of water to give a paste. The obtained paste was applied to a copper core, which was then dried at 140°C to produce a negative electrode 12. To the negative electrode core, a negative electrode lead 15 made of copper was connected by ultrasonic welding.

[0053] The positive electrode and negative electrode were rolled up in a spiral fashion, with a belt-shaped microporous separator 13 made of polypropylene interposed therebetween having a larger width than the both electrode plates, thereby constructing an electrode assembly. The electrode assembly was placed in a battery container 18, with polypropylene insulating plates 16 and 17 respectively disposed at the top and bottom thereof.

[0054] After a step was formed at the upper portion of the battery container 18, a mixed solution of ethylene carbonate and dimethoxyethane at a volume ratio of 1:1 with 1 mol/L LiClO_4 dissolved therein was injected into the battery container 18 as a non-aqueous electrolyte. The opening of the battery container 18 was sealed by a sealing plate 19 having a positive electrode terminal 20, thereby completing the fabrication of a cylindrical battery.

(iii) Evaluation of capacity characteristics

[0055] Charging (a reaction in which lithium ions are intercalated into the alloy particles) was performed on the test cell at a constant current of 0.5 mA/cm^2 until the terminal voltage became 0 V. Next, discharging (a reaction in which lithium ions are released from the alloy particles) was performed at a current of 0.5 mA/cm^2 until the terminal voltage became 1.5 V. Then, the discharge capacity (C_{ini}) was determined. Also, the ratio of the discharge capacity with respect to the charge capacity ($R_{\text{disc/c}}$) was determined in percentage. A low value of the percentage $R_{\text{disc/c}}$ indicated that there was a great occurrence of the irreversible reaction during the initial charging, that is, there was a large electrochemically irreversible capacity.

(iv) Evaluation of high-rate discharge characteristics and cycle life

[0056] The cylindrical battery was charged at a constant current of 0.2 C (5-hour rate) at 20°C until the battery voltage became 4.2 V and, thereafter, charged at a constant voltage of 4.2 V. Then, the first discharging was performed at a constant current of 0.2 C until the battery voltage became 3.0 V. In the second and later charging/discharging, the battery was charged under the same conditions as previously used, and discharged at a constant current of 2 C (0.5-hour rate) until the battery voltage became 3.0 V. The discharge capacity during the second discharging at a current of 2 C was divided by the capacity during the first discharging at a current of 0.2 C, and this was multiplied by 100 to determine a high-rate discharge ratio ($R_{2\text{C}/0.2\text{C}}$). It could be said that the closer the high-rate discharge ratio $R_{2\text{C}/0.2\text{C}}$ was to 100, the more excellent the high-rate discharge characteristics of the battery were. Further, the ratio of the discharge capacity at the 100th cycle to the discharge capacity at the 1st cycle ($R_{1\text{st}/100\text{th}}$) was determined in

percentage as the cycle retention rate. It could be said that the closer the cycle retention rate $R_{1st/100th}$ was to 100, the more excellent the cycle characteristics of the battery were.

[0057] In the following, the method of producing alloy particles is described in detail; however, the alloy particles that can be used in the present invention are not limited thereto.

Examples 1 to 6

[0058] Alloy particles were synthesized in the following manner.

[0059] Bulky simple substance materials were mixed at a predetermined ratio according to the material composition (Ti_2Sn) shown in Table 1. The mixture thus obtained was cast with an arc melting furnace.

[0060] Subsequently, spherical alloy particles were yielded from the obtained cast alloy by using a gas atomization process.

[0061] In the gas atomization process, the diameter of the jet nozzle was 1 mm ϕ and the gas jet pressure was 100 kgf/cm².

[0062] As the jet gas, an argon gas containing 1% oxygen (Example 1), an argon gas containing 3% oxygen (Example 2), an argon gas containing 5% oxygen (Example 3), a nitrogen gas containing 1% oxygen (Example 4), a nitrogen gas containing 3% oxygen (Example 5) or a nitrogen gas containing 5% oxygen (Example 6) was used.

[0063] The alloy particles obtained by the gas atomization process were sifted through a 45 micron mesh sieve to give powders having a mean particle size of 28 μm .

[0064] X-ray diffraction analysis of the above-described alloy particles confirmed the existence of the phases A and phases B having the compositions shown in Table 1. Further, electron microprobe analysis (EPMA) of the cross sections of the particles also confirmed the existence of the phases A and phases B having the compositions shown in Table 1.

[0065] Then, an oxygen content W_{ao} and a nitrogen content W_{an} in the phase A, as well as an oxygen content W_{bo} and a nitrogen content W_{bn} in the phase B were determined using a transmission electron microscope (TEM) and electron energy loss spectroscopy (EELS). More specifically, each of the oxygen content and the nitrogen content was determined by observing several points at a cross section of each particle by means of TEM while analyzing the same by EELS and converting the resulting element ratio into the weight ratio. The result is shown in Table 1.

[0066] The oxygen content W_o in the alloy particles was determined by an infrared absorption method according to JIS Z2613. Also, the nitrogen content W_n in the alloy particles was determined by a thermal conductivity method according to JIS G1228. The result is shown in Table 1.

Table 1

	Material Composition	Gas	Phase A			Phase B			W _n (wt%)	W _o + W _n (wt%)
			Composition	W _{ao} (wt%)	W _{an} (wt%)	Composition	W _{bo} (wt%)	W _{bn} (wt%)		
Ex. 1	Ti ₃ Sn	Ar + O ₂ (1%)	Sn	0.09	0.02	Ti ₃ Sn	0.70	0.23	0.31	1.14
Ex. 2		Ar + O ₂ (3%)		0.11	0.03		1.09	0.31	0.38	1.61
Ex. 3		Ar + O ₂ (5%)		0.15	0.02		1.58	0.24	0.35	2.28
Ex. 4		N ₂ + O ₂ (1%)		0.07	0.11		0.84	2.01	2.34	3.31
Ex. 5		N ₂ + O ₂ (3%)		0.10	0.15		1.19	3.27	3.55	4.86
Ex. 6		N ₂ + O ₂ (5%)		0.13	0.17		2.13	3.42	3.67	6.01
Com. Ex. 1		Ar		0.02	0.01		0.05	0.21	0.25	0.36
Com. Ex. 2		Ar + O ₂ (8%)		3.47	0.05		7.15	0.18	0.38	11.06
Com. Ex. 3		N ₂ + O ₂ (8%)		5.99	0.29		5.22	10.83	14.33	25.67
Com. Ex. 4	FeSi	Ar + O ₂ (1%)	Si	2.92	0.48	FeSi ₂	4.87	0.11	0.61	8.46
Com. Ex. 5	FeSn ₂		Sn	2.03	0.07	FeSn	3.33	0.40	0.48	5.85
Com. Ex. 6	NiAl		Al	7.21	0.30	NiAl	4.09	0.28	0.64	11.96
Com. Ex. 7	FeSi	N ₂ + O ₂ (1%)	Si	1.95	4.00	FeSi ₂	4.79	0.57	4.64	11.55
Com. Ex. 8	FeSn ₂		Sn	8.29	0.31	FeSn	5.01	5.59	5.99	19.39
Com. Ex. 9	NiAl		Al	3.37	1.78	NiAl	2.36	2.99	4.89	10.83

[0067] In Table 1, the phase A of each of Examples 1 to 6 contained almost no oxygen and nitrogen, whereas the phase B contained large amounts of oxygen and nitrogen. This was presumably because Ti had reacted preferentially with oxygen and nitrogen. Additionally, the reason why the alloy particles also contained nitrogen even in the case of using the jet gas containing no nitrogen was probably due to the fact that the starting materials contained a trace amount of nitrogen.

[0068] Table 2 shows the results of the evaluation of the test cells and cylindrical batteries fabricated using the alloy particles.

10

15

20

25

30

35

40

45

50

55

Table 2

	C _{int} mAh/g	R _{dis/c}		R _{2c/0.2c}		R _{100th/1st}	
		%		%		%	
Ex. 1	428	83		91		89	
Ex. 2	431	79		93		92	
Ex. 3	444	77		94		95	
Ex. 4	433	80		93		91	
Ex. 5	439	77		95		94	
Ex. 6	446	74		97		97	
Com. Ex. 1	419	88		75		79	
Com. Ex. 2	394	53		94		83	
Com. Ex. 3	372	49		96		87	
Com. Ex. 4	702	57		84		70	
Com. Ex. 5	536	55		87		84	
Com. Ex. 6	677	59		86		55	
Com. Ex. 7	693	43		88		68	
Com. Ex. 8	524	50		84		72	
Com. Ex. 9	654	47		83		51	

[0069] It was shown that each of the batteries of Examples 1 to 6 had a high discharge capacity and was excellent in high-rate discharge characteristics as well as cycle characteristics.

Comparative Examples 1 to 3

[0070] Spherical alloy particles were obtained in the same manner as in Example 1 except that the types of the jet gases used in the gas atomization process were changed to those shown in Table 1.

[0071] As the jet gas, an argon gas (Comparative Example 1), an argon gas containing 8% oxygen (Comparative Example 2) or a nitrogen gas containing 8% oxygen (Comparative Example 3) was used.

[0072] The obtained alloy particles were analyzed in the same manner as in Example 1. The results are shown in Table 1. Also, the test cells and cylindrical batteries fabricated using the alloy particles were evaluated in the same manner as in Example 1. The results are shown in Table 2.

[0073] In Table 1, in the case of the TiSn alloy synthesized by the gas atomization process using only the Ar gas containing neither oxygen nor nitrogen (Comparative Example 1), the oxygen content and the nitrogen content were low in the alloy particles, 0.11 wt% and 0.25 wt%, respectively. Further, the battery of Comparative Example 1, while having a high discharge capacity, was inferior to conventional lithium ion batteries in high-rate discharge characteristics and cycle life.

[0074] On the other hand, in the case of using the argon gas containing 8% oxygen (Comparative Example 2) and the nitrogen gas containing 8% oxygen (Comparative Example 3), the oxygen content and the nitrogen content each significantly increased in the alloy particles. However, as shown in Table 2, the initial ratio of the discharge capacity with respect to the charge capacity ($R_{disc/c}$) decreased. This was presumably because the oxygen content and nitrogen content in the phase A became so high that a large portion of the active phase A (Sn, in this case) was either oxidized or nitrided. In order for such phase A to absorb lithium ion, Sn was required to be reduced to a metallic state. This was considered to have resulted in an increased irreversible capacity.

Comparative Examples 4 to 6

[0075] Cast alloys were obtained in the same manner as in Example 1 except that granular simple substance materials were mixed at a predetermined ratio according to the material compositions shown in Table 1: FeSi (Comparative Example 4), FeSn₂ (Comparative Example 5) or NiAl (Comparative Example 6). Spherical alloy particles were yielded from the obtained cast alloy by using a gas atomization process under the same conditions as in Example 1.

[0076] The obtained alloy particles were analyzed in the same manner as in Example 1. The results are shown in Table 1. Also, the test cells and cylindrical batteries fabricated using the alloy particles were evaluated in the same manner as in Example 1. The result is shown in Table 2.

[0077] In each case of the alloy particles of Comparative Examples 4 to 6, the phase B did not contain Ti, Zr or rare earth elements. Therefore, as shown in Table 1, each of the oxygen content and the nitrogen content was high in the phase A, and the initial ratio of the discharge capacity with respect to the charge capacity ($R_{disc/c}$) was significantly decreased.

Examples 7 to 12

[0078] Granular simple substance materials were mixed at a predetermined ratio according to the material composition shown in Table 3: CuZrSi₂. The mixture thus obtained was cast with an arc melting furnace. Spherical alloy particles were yielded from the obtained cast alloy by using a gas atomization process under the same conditions as in Examples 1 to 6.

[0079] The obtained alloy particles were analyzed in the same manner as in Examples 1 to 6. The results are shown in Table 3. Also, the test cells and cylindrical batteries fabricated using the alloy particles were evaluated in the same manner as in Examples 1 to 6. The results are shown in Table 4.

Table 3

	Material Composition	Ambience	Phase A		Phase B			W _n (wt%)	W _o + W _n (wt%)
			Composition	W _{ao} (wt%)	W _{an} (wt%)	Composition	W _{bo} (wt%)	W _{bn} (wt%)	
Ex. 7	CuZrSi ₂	Ar + O ₂ (1%)	Si	0.08	0.02	CuZr	1.72	0.27	1.86
Ex. 8		Ar + O ₂ (3%)		0.11	0.02		1.90	0.28	2.04
Ex. 9		Ar + O ₂ (5%)		0.13	0.03		3.00	0.41	3.24
Ex. 10		N ₂ + O ₂ (1%)		0.08	0.11		1.47	2.53	1.57
Ex. 11		N ₂ + O ₂ (3%)		0.10	0.16		1.81	2.90	1.96
Ex. 12		N ₂ + O ₂ (5%)		0.14	0.19		2.32	3.25	2.51
Ex. 13	NiLaGa	N ₂	Ga	0.15	0.21	NiLa	1.95	2.80	2.12
Ex. 14	NiCeIn ₂		In	0.13	0.25		2.23	3.14	2.43
									5.84

Table 4

	C _{ini} mAh/g	R _{disc/e}		R _{2c/0.2c}		R _{100in/1.5s}	
		%		%		%	
Ex. 7	643	84		90		87	
Ex. 8	651	82		94		91	
Ex. 9	659	79		95		94	
Ex. 10	648	82		91		89	
Ex. 11	653	78		94		92	
Ex. 12	668	75		96		95	
Ex. 13	512	72		91		94	
Ex. 14	693	78		94		97	

[0080] In each case of the alloy particles of Examples 7 to 12, the oxygen content W_o and nitrogen content W_n contained in the entire alloy particles satisfied $0 < W_o < 10 \text{ wt\%}$, $0 < W_n < 10 \text{ wt\%}$ and $0.5 \text{ wt\%} \leq W_o + W_n \leq 10 \text{ wt\%}$. Also, the batteries of Examples 7 to 12 each had a high capacity, excellent high-rate discharge characteristics and long life.

5 Examples 13 to 14

[0081] Granular simple substance materials were mixed at a predetermined ratio according to the material compositions shown in Table 3: NiLaGa or NiCeIn₂. The mixture thus obtained was cast with an arc melting furnace. Alloy particles were yielded from the obtained cast alloy by using water atomization process. The water atomization was performed under a nitrogen atmosphere. The oxygen and nitrogen incorporated into the alloy in the water atomization process were supplied from the oxygen and nitrogen dissolved in water and also from the oxygen generated by the oxidation of water at the time of the collision of water and a molten metal.

[0082] In the water atomization process, water with a jet pressure of 800 kgf/cm² was collided with the molten metal of the alloy to rapidly cool and pulverize the alloy. The alloy particles thus obtained were sifted through a 45 micron mesh sieve to give powders having a mean particle size of 20 μm .

[0083] The obtained alloy particles were analyzed in the same manner as in Example 1. The results are shown in Table 3. Also, the test cells and cylindrical batteries fabricated using the alloy particles were evaluated in the same manner as in Example 1. The results are shown in Table 4.

[0084] Analysis of the cross sections of the particles by means of EPMA revealed that an oxide film having a mean thickness of approximately 18 nm was formed on the surface of each particle synthesized by the water atomization process.

[0085] From Table 3, it was shown that considerably larger amounts of oxygen and nitrogen were incorporated into the phase B, than into the phase A.

[0086] In each case of the alloy particles of Examples 13 to 14, the oxygen content W_o and nitrogen content W_n contained in the entire alloy particles satisfied $0 < W_o < 10 \text{ wt\%}$, $0 < W_n < 10 \text{ wt\%}$ and $0.5 \text{ wt\%} \leq W_o + W_n \leq 10 \text{ wt\%}$. Also, the batteries of Examples 13 to 14 each had a high capacity, excellent high-rate discharge characteristics and long life.

[0087] In Examples 1 to 14 described above, observation with TEM and electron beam diffraction analysis revealed that the phase B containing large amounts of oxygen and nitrogen was in a low crystalline or amorphous state. A portion of the phase B formed fine oxides and nitrides, thereby producing many grain boundaries in the phase. Because of this, the conductive network of lithium ion increased within the particles, good lithium ion conductivity was achieved and the high-rate discharge characteristics of the battery were improved. Moreover, since the phase B was suited to absorb the stress caused by the expansion and contraction of the phase A, the cycle life of the battery was also improved. While the incorporation of oxygen into the phase B was able to provide the effect of the stress relaxation to some extent, the additional incorporation of nitrogen into the phase B was considered to have significantly improved the effect of the stress relaxation.

Examples 15 to 19

[0088] Alloy particles were synthesized in the following manner.

[0089] Into a stainless steel pot mill (capacity 500 ml) containing therein 25 stainless steel balls (diameter 4.8 cm), simple substance materials having a particle size of not more than 45 μm were supplied at a predetermined ratio according to the material compositions shown in Table 5: TiPb (Example 15), ZrSb₂ (Example 16), TiCoBi (Example 17), Ti₂Sn (Example 18) or TiSi₂ (Example 19).

[0090] In Examples 15 to 17, predetermined additives having a particle size of not more than 45 μm shown in Table 5 were also supplied into the pot mill at the respective ratios shown in Table 5 with respect to the total amount of the materials and additives. In the case of adding fluorine to the alloy, a granular powder of LiF was used as the additive.

[0091] The total amount of the materials to be supplied into the pot mill was set at 15 g, including the additive.

[0092] An argon gas containing 3% oxygen was charged in the pot mill.

[0093] The pot mill was operated at a constant revolution of 60 rpm for 10 days. As a result, alloy particles having a mean particle size of approximately 0.8 μm were obtained.

[0094] X-ray diffraction analysis of the obtained alloy particles revealed that each alloy particles had a broad diffraction-pattern and thus was in a low crystalline-or amorphous state. Further, the phase structures of the alloy particles were analyzed by using the above diffraction patterns and TEM. As a result, it was found that all the powders had the phases A and the intermetallic compound phases B shown in Table 5.

[0095] Then, the obtained alloy particles were analyzed in the same manner as in Example 1. The results are shown in Table 5. Also, the test cells and cylindrical batteries fabricated using the alloy particles were evaluated in the same manner as in Example 1. The results are shown in Table 6.

Table 5

	Material Composition	Ambience	Additive	Added amount wt%	Phase A			Phase B				Wn (wt%)	Wo + Wn (wt%)
					Composition	Wao (wt%)	Wan (wt%)	Composition	Wbo (wt%)	Wbn (wt%)	Wo (wt%)		
Ex. 16	TiPb	Ar + O ₂ (3%)	LiF	1.00	Pb	0.09	0.02	PbTi ₄	0.93	0.30	1.08	0.34	1.42
Ex. 16	ZrSb ₂		S	0.50	Sb	0.10	0.03	SbZr	1.48	0.15	1.62	0.22	1.84
Ex. 17	TiCoBi		P	1.00	Bi	0.13	0.02	CoTi	2.35	0.11	2.54	0.19	2.73
Ex. 18	Ti ₂ Sn		-	-	Sn	0.12	0.04	Ti ₂ Sn ₃	3.48	0.42	3.67	0.55	4.22
Ex. 19	TiSi ₂		-	-	Si	0.10	0.02	TiSi	4.10	0.35	4.26	0.43	4.69
Ex. 20	TiPb	N ₂ + O ₂ (3%)	LiF	1.00	Pb	0.17	0.21	PbTi ₄	2.46	3.41	2.64	3.67	6.31
Ex. 21	ZrSb ₂		S	0.50	Sb	0.11	0.12	SbZr	3.14	4.10	3.17	4.26	7.42
Ex. 22	TiCoBi		P	1.00	Bi	0.14	0.20	CoTi	3.05	2.88	3.22	3.12	6.34
Ex. 23	Ti ₂ Sn		-	-	Sn	0.16	0.13	Ti ₂ Sn ₃	4.09	5.12	4.28	5.29	9.57
Ex. 24	TiSi ₂		-	-	Si	0.14	0.17	TiSi	4.53	4.62	4.69	4.87	9.56
Com. Ex. 10	TiPb	Ar	LiF	1.00	Pb	0.02	0.01	PbTi ₄	0.14	0.10	0.19	0.14	0.33
Com. Ex. 11	ZrSb ₂		S	0.50	Sb	0.03	0.04	SbZr	0.11	0.21	0.17	0.26	0.43
Com. Ex. 12	TiCoBi		P	1.00	Bi	0.02	0.03	CoTi	0.17	0.16	0.21	0.22	0.43
Com. Ex. 3	Ti ₂ Sn		-	-	Sn	0.04	0.05	Ti ₂ Sn ₃	0.19	0.11	0.26	0.18	0.44
Com. Ex. 14	TiSi ₂		-	-	Si	0.03	0.04	TiSi	0.08	0.14	0.14	0.19	0.33
Com. Ex. 16	TiPb	Air	LiF	1.00	Pb	3.90	0.22	PbTi ₄	6.42	9.01	10.34	9.24	19.58
Com. Ex. 10	ZrSb ₂		S	0.50	Sb	6.11	0.31	SbZr	4.13	10.01	9.28	10.35	19.63
Com. Ex. 17	TiCoBi		P	1.00	Bi	4.73	0.18	CoTi	7.57	9.26	12.36	9.47	21.82
Com. Ex. 18	Ti ₂ Sn		-	-	Sn	6.22	0.24	Ti ₂ Sn ₃	4.91	11.09	11.06	11.38	22.44
Com. Ex. 10	TiSi ₂		-	-	Si	5.39	3.71	TiSi	2.27	6.33	7.69	10.08	17.77

Table 6

	C _{ini} mAh/g	R _{disc/c}		R _{sc/o.sc}		R _{100th/1st}	
		%		%		%	
Ex. 15	521	83		91		89	
Ex. 16	724	80		93		87	
Ex. 17	536	77		92		91	
Ex. 18	426	80		94		97	
Ex. 19	719	77		93		94	
Ex. 20	534	74		95		90	
Ex. 21	694	79		94		92	
Ex. 22	544	74		91		93	
Ex. 23	451	79		96		98	
Ex. 24	720	73		94		95	
Com. Ex. 10	551	85		83		55	
Com. Ex. 11	742	82		85		64	
Com. Ex. 12	549	80		81		66	
Com. Ex. 13	437	84		78		78	
Com. Ex. 14	736	79		74		61	
Com. Ex. 15	511	50		84		49	
Com. Ex. 16	694	47		86		60	
Com. Ex. 17	512	49		85		58	
Com. Ex. 18	396	59		83		70	
Com. Ex. 19	679	43		84		60	

Examples 20 to 24

[0096] The same operations as in Examples 15 to 19 were performed except that a nitrogen gas containing 3% oxygen was charged in the pot mill, thereby obtaining alloy particles having a mean particle size of approximately 0.8 μm . X-ray diffraction analysis of the obtained alloy particles revealed that the alloy particles each had a broad diffraction pattern and thus was in a low crystalline or amorphous state. Further, the phase structures of the alloy particles were analyzed by using the above diffraction patterns and TEM. As a result, it was found that all the powders had the phases A and the intermetallic compound phases B shown in Table 5.

[0097] Then, the obtained alloy particles were analyzed in the same manner as in Example 1. The results are shown in Table 5. Also, the test cells and cylindrical batteries fabricated using the alloy particles were evaluated in the same manner as in Example 1. The results are shown in Table 6.

Comparative Examples 10 to 14

[0098] The same operations as in Examples 15 to 19 were performed except that an argon gas having a purity of 99.999% was charged in the pot mill, thereby obtaining alloy particles having a mean particle size of approximately 0.8 μm . X-ray diffraction analysis of the obtained alloy particles revealed that the alloy particles each had a broad diffraction pattern and thus was in a low crystalline or amorphous state. Further, the phase structures of the alloy particles were analyzed by using the above diffraction patterns and TEM. As a result, it was found that all the powders had the phases A and the intermetallic compound phases B shown in Table 5.

[0099] Then, the obtained alloy particles were analyzed in the same manner as in Example 1. The results are shown in Table 5. Also, the test cells and cylindrical batteries fabricated using the alloy particles were evaluated in the same manner as in Example 1. The results are shown in Table 6.

[0100] The reason why the cycle characteristics were insufficient in each case of Comparative Examples 10 to 14 was presumably because the alloy particles contained almost no oxygen and nitrogen, so that there were few grain boundaries within the particles and the expansion stress was difficult to be relaxed.

Comparative Examples 15 to 19

[0101] The same operations as in Examples 15 to 19 were performed except that air was charged in the pot mill, thereby obtaining alloy particles having a mean particle size of approximately 0.8 μm . X-ray diffraction analysis of the obtained alloy particles revealed that the alloy particles each had a broad diffraction pattern and thus was in a low crystalline or amorphous state. Further, the phase structures of the alloy particles were analyzed by using the above diffraction patterns and TEM. As a result, it was found that all the powders had the phases A and the intermetallic compound phases B shown in Table 5.

[0102] Then, the obtained alloy particles were analyzed as in Example 1. The results are shown in Table 5. Also, the test cells and cylindrical batteries fabricated using the alloy particles were evaluated in the same manner as in Example 1. The results are shown in Table 6.

[0103] In Table 5, larger amounts of oxygen and nitrogen were contained in the phase B in each case of Examples 15 to 24, as compared with Comparative Examples 10 to 14.

[0104] In Table 6, the batteries of Examples 15 to 24 were superior in high-rate discharge characteristics and life characteristics. On the other hand, the batteries of Comparative Examples 10 to 14, which contained the alloy particles synthesized under an Ar gas atmosphere of high purity, were insufficient in life characteristics and high-rate discharge characteristics.

[0105] It was also shown that the batteries of Comparative Examples 15 to 19, which contained the alloy particles synthesized under an air atmosphere, had a large irreversible capacity because the oxygen content and the nitrogen content were too large in the phase A of the alloy particles.

[0106] It should be noted that most of the additives were detected only in the phase B.

[0107] As described above, the batteries using in the negative electrodes, the alloy particles of Examples in accordance with the present invention had a higher capacity and exhibited superior cycle characteristics as well as high-rate discharge characteristics, as compared with the batteries of Comparative Examples. Moreover, in the case of the alloy particles having excellent properties, not less than 70 wt% of the total amount of oxygen and nitrogen was contained in the phase B. Also, in the case of the alloy particles yielding a battery having high capacity and superior high-rate discharge capacity and long life, the oxygen content W_o and the nitrogen content W_n satisfied $0 < W_o < 10 \text{ wt\%}$, $0 < W_n < 10 \text{ wt\%}$ and $0.5 \text{ wt\%} \leq W_o + W_n \leq 10 \text{ wt\%}$.

[0108] Although $\text{LiMn}_{1.8}\text{Co}_{0.2}\text{O}_4$ was used as the positive electrode in the above-described examples, the same effect can certainly be obtained by using LiMn_2O_4 , LiCoO_2 , LiNiO_2 and the like.

Industrial Applicability

[0109] As described above, according to the present invention, it is possible to obtain a highly reliable non-aqueous electrolyte secondary battery which has high capacity, long life as well as excellent high-rate discharge characteristics and which is free from short-circuit due to lithium dendrites.

Claims

1. A non-aqueous electrolyte secondary battery comprising: a positive electrode capable of absorbing and desorbing lithium ion; a negative electrode capable of absorbing and desorbing lithium ion; and a non-aqueous electrolyte containing a lithium salt,
 said negative electrode comprising: an alloy particle containing at least two selected from the group consisting of metal elements and semimetal elements; and one selected from the group consisting of oxygen and nitrogen,
 wherein said alloy particle has a phase A capable of electrochemically absorbing and desorbing lithium ion and a phase B which is incapable of electrochemically absorbing and desorbing lithium ion and has lithium ion conductivity or lithium ion permeability and
 wherein the total of an oxygen content W_{ao} and a nitrogen content W_{an} is less than 0.5 wt% in said phase A and the total of an oxygen content W_{bo} and a nitrogen content W_{bn} is not less than 1.0 wt% in said phase B.
2. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said phase A contains at least one selected from the group consisting of Sn, Si, Al, Ga, In, Pb, Sb and Bi and wherein said phase B contains at least one selected from the group consisting of Ti, Zr and rare earth elements.
3. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said phase A is surrounded by said phase B.
4. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said oxygen content W_{ao} and said nitrogen content W_{an} in said phase A and said oxygen content W_{bo} and said nitrogen content W_{bn} in said phase B satisfy $\{(W_{bo}+W_{bn})/(W_{ao}+W_{an})\}>4$.
5. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein an oxygen content W_o and a nitrogen content W_n in said alloy particle satisfy $0<W_o<10$ wt%, $0<W_n<10$ wt% and $0.5 \text{ wt}\% \leq W_o+W_n \leq 10 \text{ wt}\%$.
6. The non-aqueous electrolyte secondary battery in accordance with claim 1, wherein said alloy particle further contains at least one selected from the group consisting of fluorine, sulfur and phosphorous and wherein the total of said oxygen content W_o , said nitrogen content W_n , and a content W_f of at least one selected from the group consisting of fluorine, sulfur and phosphorous, is 0.5 to 10 wt% in said alloy particle.

FIG. 1

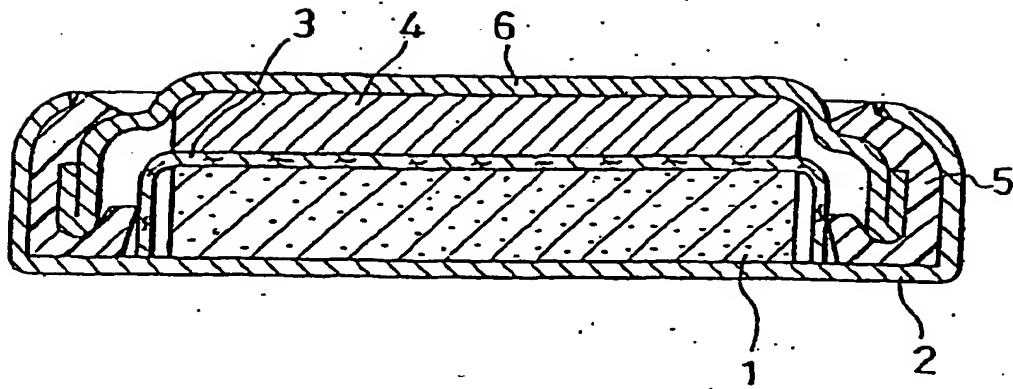
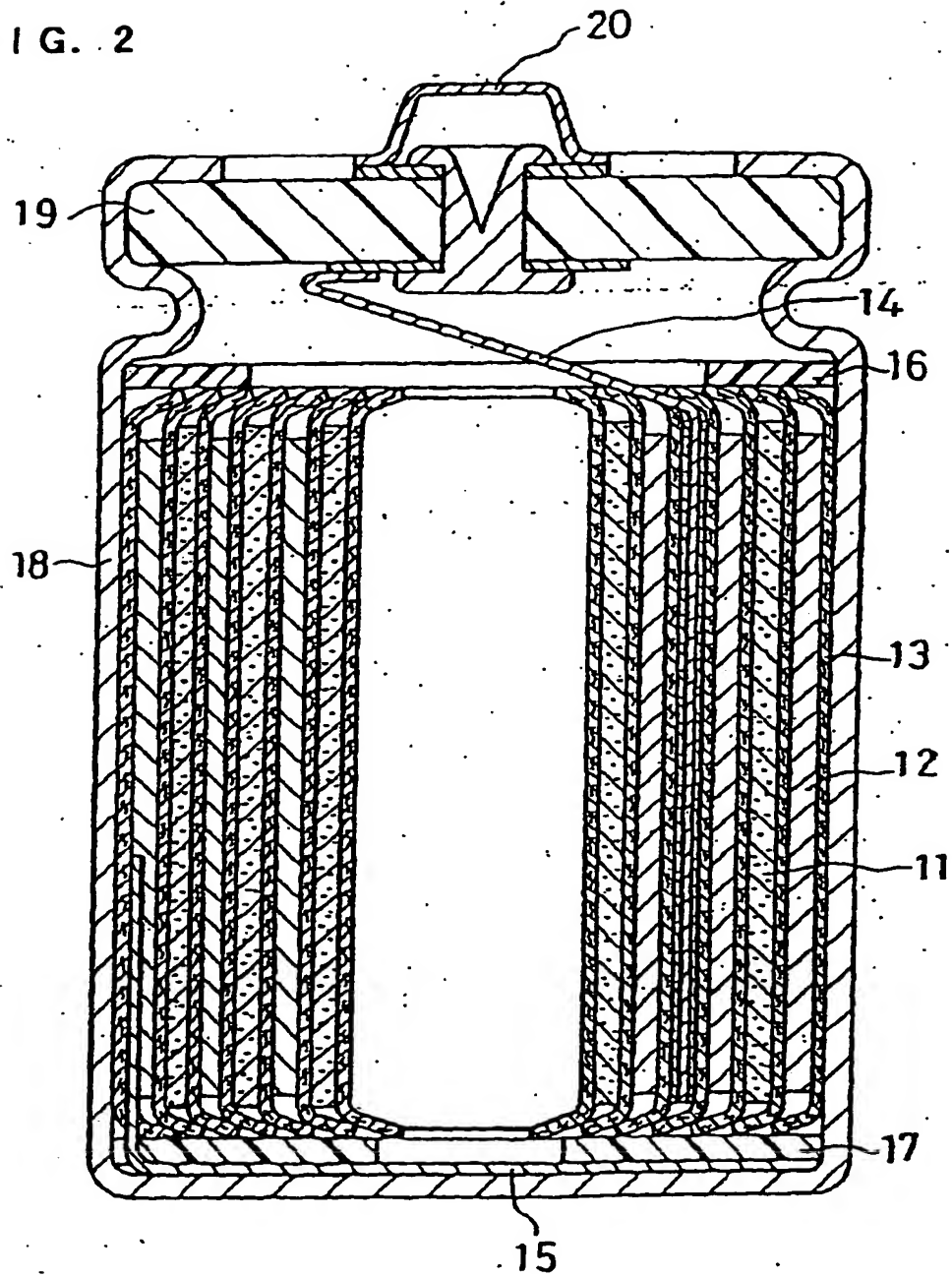


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/06189

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl.⁷ H01M4/38, 4/02, 10/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.⁷ H01M4/02, 4/38-4/46, 10/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926-1996 Jitsuyo Shinan Toroku Koho 1996-2001

Kokai Jitsuyo Shinan Koho 1971-2001 Toroku Jitsuyo Shinan Koho 1994-2001

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11-86854 A (Hitachi, Ltd.), 30 March, 1999 (30.03.99), (Family: none)	1-6
A	JP 11-86853 A (Hitachi, Ltd.), 30 March, 1999 (30.03.99), (Family: none)	1-6
A	JP 2000-173611 A (Matsushita Electric Ind. Co., Ltd.), 23 June, 2000 (23.06.00), (Family: none)	1-6

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search
02 October, 2001 (02.10.01)

Date of mailing of the international search report
09 October, 2001 (09.10.01)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.